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SEQUENTIAL DEPOSITION OF COPPER ON SOLID
GOLD (111): A STATISTICAL MODEL

by

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Sequential Deposition of Copper on Solid Gold (111):A Statistical Model

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Abstract

Phase transitions occurring during electrode processes have been studied using a model in which the electrode is a planar wall with sticky adsorption sites. This model is used to explain the underpotential deposition (UPD) of copper on gold (111) in the presence of bisulfate ions. The model assumes that the bisulfate ions form a template for the adsorption of the first $2/3$ of a monolayer of copper onto a honeycomb lattice. The centers of the hexagons that form the honeycomb are occupied by the bisulfate. In the absence of copper the bisulfate is desorbed as the electrode becomes more negatively charged, and for that reason the template 'melts' when the fraction of occupied sites drops below a certain critical value, which is estimated using the hard hexagon model of Baxter. We assume strong copper-bisulfate coadsorption, so that in the presence of a sufficiently large amount of Cu the template is reconstructed. Our model explains the qualitative features of the voltammogram and makes definite predictions for the structures that should be observed.

1 Theory

Voltammograms[1] of underpotential deposited films on perfect single crystal surfaces [2, 3] contain sharp spikes [4, 5]. In earlier work, we discussed the possibility of explaining these spikes as the result of first order phase transitions occurring in the surface [6, 7]. There are a number of conditions that have to be met to obtain experimentally sharp spikes in a voltammogram. These include chemical equilibrium, the degree of perfection of the substrate (a single crystal in most cases), and the scanning rate of the voltammogram. Ideally perfect single

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crystal surfaces with large domains, fast kinetics and diffusion should produce narrow spikes. Slow voltage scanning rates would be best to observe these spikes. The area under the spike is proportional to the charge transferred, not to the coverage of the surface, because the charge per adatom on the surface is not necessarily an entire number equal to the stoichiometric electrovalence [8]. However, sharp spikes are not the only interesting features of the voltammograms. New advances in ex and in situ surface analysis make it possible to determine and discriminate the origin of broadening effects. The case of the UPD of Cu on Au(111) in the presence of H_2SO_4 has been extensively studied in recent times both experimentally [9, 10, 11, 12, 13, 14, 16, 17, 18, 19] and theoretically [20]. The picture that emerges shows that the broad foot observed in the voltammogram is due neither to kinetic effects, nor to domain size effects, nor to surface reconstruction, and it is completely reversible. Therefore it is due to genuine statistical effects that have to be accounted for. In the present communication we amplify a previously proposed model [21] to include the dynamics of the HSO_4^- adsorption-desorption process. We find that the broad foot of the first spike in the Cu-Au voltammogram can be explained by a second order surface phase transition, similar to the so called hard hexagon phase transition [22].

We assume that in the initial stages of the process there is a strong coadsorption of copper with the bisulfate. At positive potentials ($V > 0.4$ volts with respect to the standard (Ag/AgCl) electrode), the bisulfate is strongly adsorbed onto the clean Au(111) surface. We assume, in accordance with chemical common knowledge, that it retains its charge, and therefore, the bisulfate-bisulfate interaction is both long ranged and repulsive. If we assume, as we have done in our previous work [21, 20], that the HSO_4^- sits in a tripod position, that is with its three oxygen atoms directly atop the Au atoms of the surface, then the adsorption of one HSO_4^- necessarily excludes nearest neighbor occupation. This makes the short ranged part of the surface interaction mathematically isomorphic to the hard hexagon problem, solved some years ago by Baxter[22]. According to this work, there will be a second order, order-disorder phase transition when

$$\theta_S \geq \theta_c = 0.2764, \quad (1)$$

where θ_S is the fraction of the Au(111) lattice adsorption sites that are occupied by the bisulfate.

Consider a model in which there are three species, which for brevity we will call E (empty sites), C (copper) and S (bisulfate). In our lattice model of the surface there is no interaction between E and the other adsorbates, S strongly repels S, and S-C and C-C are strongly attractive. Models in which three components are adsorbed were recently discussed in the literature [23, 24, 25, 26], but only nearest

neighbor configurations were taken into consideration. In our case at least second neighbors need to be included.

Following our earlier work on the sticky site model [6, 7], we define a site adsorption fugacity z_x for the adsorption of either of the species $x = S, C$, which is the product of the contact density $\rho_x^0(0, \Psi)$ and the sticky parameter λ_x , which in our case [1] is the exponential of the electrochemical binding potential divided by kT

$$z_x = \lambda_x(\psi) \rho_x^0(0, \psi) = e^{\mu_x/kT}. \quad (2)$$

We assume the simple, Butler-Volmer like [1] ansatz for the fugacity

$$z_S = e^{\mu_S/kT} = e^{-\zeta_S e(\psi - \psi_S)/kT}, \quad (3)$$

where the electrosorption valency of the bisulfate is $\zeta_S = -1$, and ψ_S is the electrosorption potential, which depends on the nature of the substrate.

The adsorption isotherm for the hard hexagon model has been derived by Joyce [27]. For the low density disordered phase a simplification of these results is achieved using the variable [28]

$$\Phi = \theta(1 - \theta) \quad (4)$$

instead of θ . For the low density phase we get

$$z_{low} = Q \left[Q_0^2 \sqrt{Q_1} + Q_2 - Q_0 \sqrt{2Q_2 \sqrt{Q_1} + 2Q_3} \right]$$

with

$$Q = \frac{1 - 5\Phi + 5\Phi^2 + \sqrt{1 - 4\Phi}(1 - 3\Phi + \Phi^2)}{8\Phi^6}$$

$$Q_0 = 1 - 5\Phi$$

$$Q_1 = Q_0(1 - \Phi)$$

$$Q_2 = \sqrt{1 - 4\Phi}(1 - 11\Phi + 33\Phi^2 - 11\Phi^3)$$

$$Q_3 = 1 - 16\Phi + 90\Phi^2 - 198\Phi^3 + 119\Phi^4 - 10\Phi^5, \quad (5)$$

and for the ordered phase

$$z_{high} = \frac{-2 + 9\Phi - 6\Phi^2 - (2 - 5\Phi)\sqrt{1 - 4\Phi}}{1 - 12\Phi + 33\Phi^2 + (5\Phi - 1)^{3/2}\sqrt{9\Phi - 1}}. \quad (6)$$

For our purposes we need an approximate representation of the occupation rate as a function of the fugacity. After some calculations and curve fitting, we get for the high density, ordered phase

$$\theta_S^{high} = \frac{0.2764 + 0.155(z_S - 11.09) + 0.01(z_S - 11.09)^2}{1 + 0.5(z_S - 11.09) + 0.03(z_S - 11.09)^2}, \quad z_S > 11.09. \quad (7)$$

while for the low density, disordered phase,

$$\theta_S^{low} = \frac{0.709z_S + 0.0079z_S^2 + 0.0011z_S^3}{1 + 3.3z_S}, \quad 0 < z_S < 11.09. \quad (8)$$

Consider now the adsorption of bisulfate onto Au(111) in the absence of copper. Using Eq.(3) with the effective charge of the adsorbed bisulfate $\zeta_S = -1$,

$$\mu_S/kT = 38.922[v - v_S^{Au}], \quad (9)$$

where we take

$$v_S^{Au} = 0.20V \quad (10)$$

and the bisulfate fugacity z_S is

$$z_S = e^{38.922[v - v_S^{Au}]} \quad (11)$$

The bisulfate is desorbed as the potential turns more negative. This is shown in figure 1. With these parameters the S lattice becomes disordered at about 0.45 V, which is when the copper starts to deposit. As long as the S template is disordered, the Cu is adsorbed randomly (probably next to the bisulfate). The transition from ordered to disordered phase should be observable by the STM or AFM techniques.

The radiotracer experiments [29] in which the adsorption of labelled S was measured are in qualitative agreement with the above results. Unfortunately, these experiments were done on polycrystalline gold.

If copper is present, it will start depositing at around $v = 0.4V$, but since the bisulfate is in its disordered phase, there should be no cooperative effects due to the copper-copper attraction on the surface, and therefore, to a first approximation we may assume that the electrodeposition of copper follows a Langmuir-like (or Frumkin-Langmuir [1]) adsorption isotherm

$$\theta_C = \frac{z_C}{1 + z_C} \quad \theta_S < \theta_S^{crit} = 0.2764 \quad (12)$$

with

$$z_C = e^{-\zeta_C e(\psi - \psi_C^{Au})/kT}, \quad (13)$$

where ψ_C^{Au} is the electrodeposition reference potential of Cu on gold (111), and ζ_C is the effective electrovalence (certainly related to the electrosorption valency) of Cu. We remark that this is the simplest possible scenario: we expect that both ψ_C^{Au} and ζ_C should change with θ_C and θ_S , but this should not alter the nature of our conclusions.

The electrosorption of bisulfate on polycrystalline copper [30] shows that it binds much more strongly than to gold. These authors quote an adsorption maximum at $v = -0.3V$. For this reason, to a first approximation, we may assume that the electrosorption potential of the bisulfate varies linearly with the amount of copper in the surface. Thus, guided also by the work of Trassatti on the influence of the anion on the potential of zero charge [31], we take

$$v_S^{Cu} < v_S^{Au}. \quad (14)$$

In our improved model, then

$$z_S = e^{-\zeta_S e(\psi - \psi_S)/kT}, \quad (15)$$

with

$$\psi_S = \psi_S^{Cu} \theta_C + (1 - \theta_C) \psi_S^{Au}, \quad (16)$$

or in volts

$$v_S = v_S^{Cu} \theta_C + (1 - \theta_C) v_S^{Au}. \quad (17)$$

In the presence of copper the bisulfate is then readsorbed. Eventually, the fraction of occupied sites will again surpass the critical value of 0.2764 (which corresponds to 83% of the occupancy of the template $\sqrt{3} \times \sqrt{3}$ lattice), and then there will be a first order transition for the copper on the honeycomb lattice of the Cu sites [32].

As was discussed in our earlier work [7], a phase transition will appear in the voltammogram as a sharp peak in the intensity I . If the scanning rate is constant and we neglect diffusion and double layer effects [1], the intensity of the current in the voltammogram can be obtained by differentiation as

$$I(v) = -\frac{\partial \theta}{\partial v} \frac{dv}{dt}. \quad (18)$$

The width of the spike will depend on a number of factors, as was mentioned earlier. In our present case it should depend on the number of defects in the template, and for that reason on the concentration of bisulfate. Figure 2 shows the voltammogram of Kolb [11]. Figure 3 shows a calculation in which the parameters have been chosen

from reasonable values, to fit the experiment qualitatively. In our model [21] we assume that the second peak of the voltammogram is due to the displacement of the adsorbed bisulfate by copper. Because of steric considerations this should be a high activation energy process. Furthermore, since it is reversible, and also from experimental evidence, we believe that the bisulfate remains adsorbed on top of the copper monolayer. This monolayer could be either ordered or disordered, depending on its coverage, as was discussed above.

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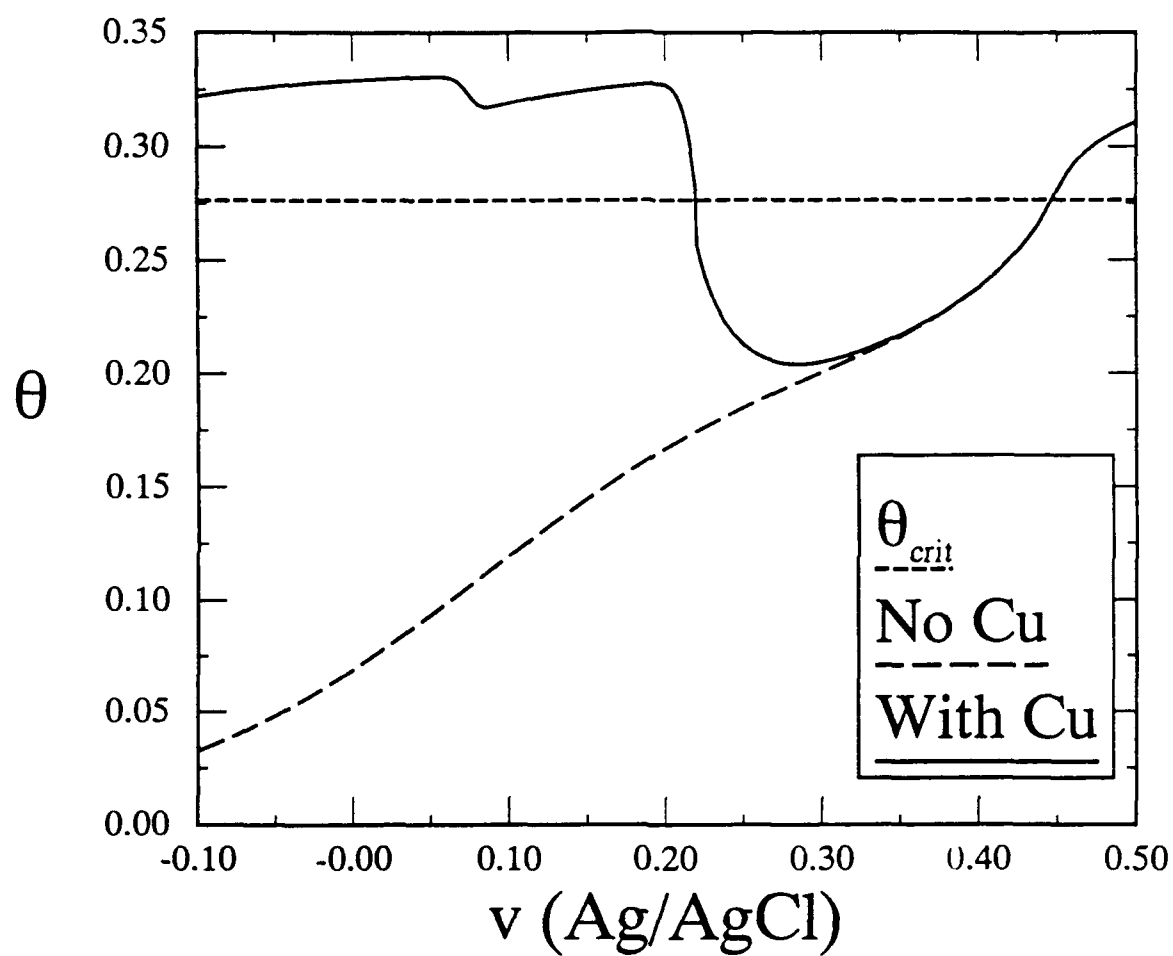


Figure 1: Fraction of occupied sites by HSO_4^- . Dotted line represents the case of a clean gold (111) surface. Solid line corresponds to our model of copper coadsorption.

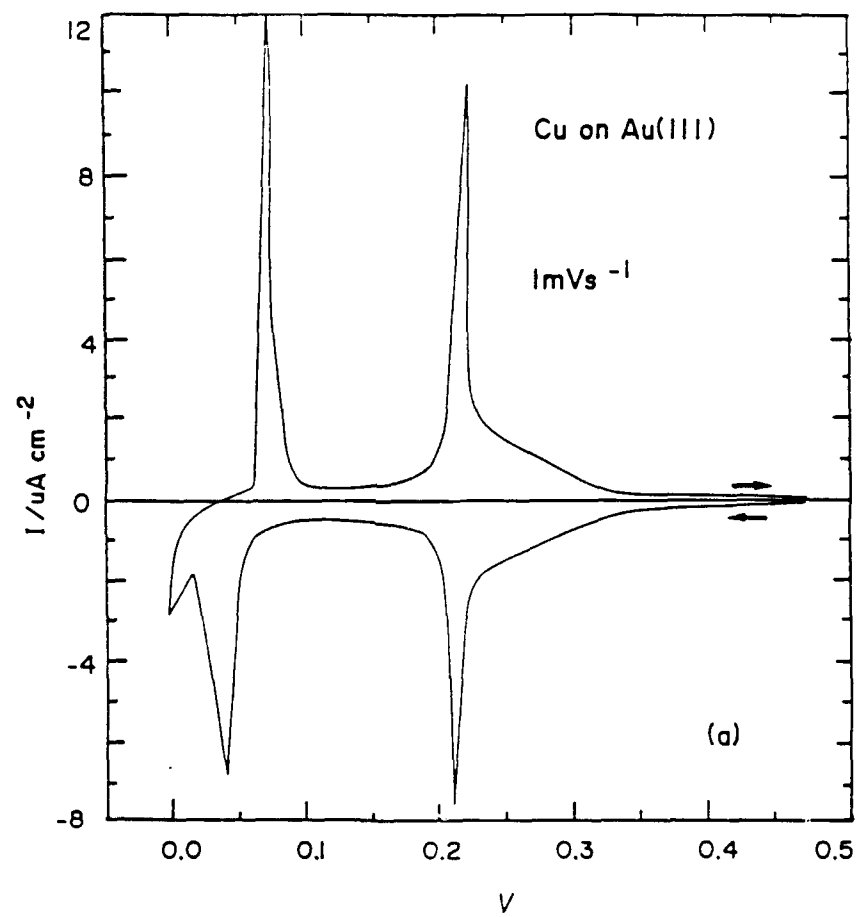


Figure 2: Kolb's voltammogram

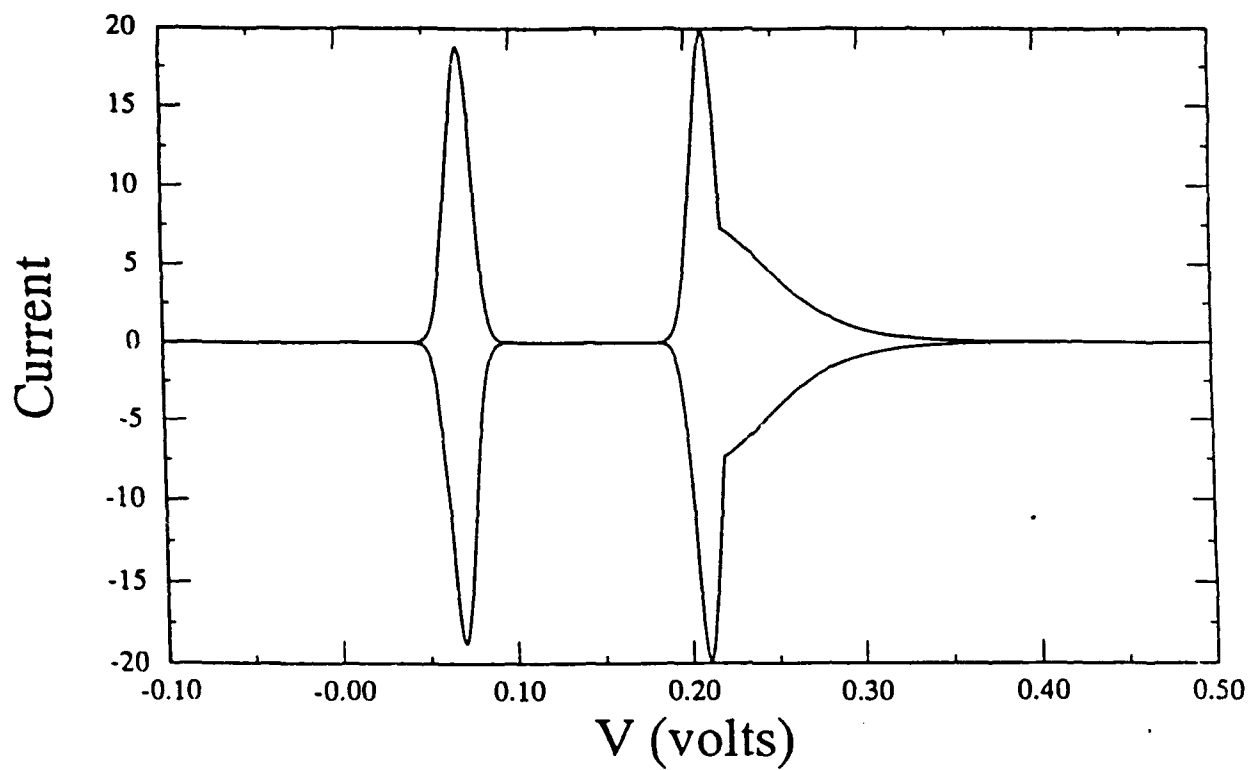


Figure 3: Ideal voltammogram for Cu UPD. The parameters were fixed so that the first peak occurs at 0.21V, the second at 0.07V, and the second order transition at 0.22V. The curves are normalized so that the areas are in a ratio 2:1, and the widths are fixed arbitrarily.